



Generalized equipartition theorem and confining walls

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Generalized equipartition theorem and confining walls

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It is shown that the generalized equipartition theorem as applied to the momentum may fail, even though the usual conditions of validity are met. This failure is linked to the nature of the confining walls, with ideal walls constituting a singular case. The corresponding analysis illustrates the use of proper sets of canonical coordinates, and the utility of canonical transformations other than point transformations. © 2015 American Association of Physics Teachers.

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I. INTRODUCTION

The generalized equipartition theorem¹ (GET) ranks among the basic results of classical statistical mechanics. Its corollaries are the theorem of equipartition (TE) for quadratic contributions to the Hamiltonian, and the statistical virial theorem. This fundamental role justifies its inclusion in several well-known statistical mechanics textbooks.^{1–3} Generally, though, its discussion is terse, with the aforementioned corollaries immediately capturing the spotlight. The literature on the GET^{4–7} and its applications⁸ is scarce as well.

This almost century-old⁹ theorem can be summarized by stating that for a given set of generalized coordinates $\{q_i, p_i\} \equiv \{x_i\}$, the following thermal average holds for any x_i :

$$\left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle = k_B T, \quad (1)$$

under the conditions⁹ that x_i becomes either zero or infinity at its two limits, and the energy becomes infinite if x_i does. (Here, H is the Hamiltonian, T is the absolute temperature, and k_B is Boltzmann's constant.)

The GET is most easily illustrated for a free particle, with $H = \sum_i p_i^2/2m$. For each Cartesian momentum the theorem yields $\langle p_i \cdot \partial H / \partial p_i \rangle = \langle p_i^2 / m \rangle = k_B T$, so that we get the usual equipartition of energy (specializing to the case of two-dimensions for simplicity)

$$\langle H \rangle = \frac{1}{2} \sum_i \left\langle \frac{p_i^2}{m} \right\rangle = \frac{1}{2} (k_B T + k_B T) = k_B T. \quad (2)$$

Along with the limited attention that the GET has received in textbook accounts, it is not emphasized that care needs to be exercised even in cases as simple as this one. Indeed, an apparently inoffensive change of perspective can lead to conflicting results. The problem arises if the Hamiltonian is expressed in terms of the modulus of the total momentum

$$H = \frac{p^2}{2m}. \quad (3)$$

Now, we are entitled to consider p as one coordinate of a certain set of generalized coordinates—a coordinate that fulfills the conditions previously stated (its limits are zero and infinity, and the energy becomes infinite as $p \rightarrow \infty$). Carrying on the argument, according to the tenets of the theorem we should expect that $\langle p \cdot \partial H / \partial p \rangle = k_B T$, and since in this case

$p \cdot \partial H / \partial p = 2H$, we are confronted with the (incorrect) result

$$\langle H \rangle = \frac{1}{2} \left\langle p \frac{\partial H}{\partial p} \right\rangle = \frac{k_B T}{2}. \quad (4)$$

Alternatively, in the language of the TE, this means that we cannot take at face value the statement “each quadratic term in the Hamiltonian averages to $k_B T/2$,” because a quadratic term is what we have in Eq. (3).

Where did we go wrong? Certainly not in considering p a valid generalized coordinate. Rather, it will be shown below that this example constitutes an instance for which the theorem is not valid, despite all its usual conditions being fulfilled. In this particular case, these conditions are not sufficient, and a proper handling of the interaction with walls is required if one wishes to recover the validity of the GET.

We will return to this example in Sec. III below. First, however, we use the harmonic oscillator as a convenient “playground.”

II. HARMONIC OSCILLATOR

As in the case of a free particle, it will suffice to work in two dimensions. We also assume an isotropic oscillator, so the Hamiltonian is

$$\begin{aligned} H &= \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{1}{2} m \omega^2 (x^2 + y^2) \\ &= \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{1}{2} m \omega^2 r^2. \end{aligned} \quad (5)$$

A careless manipulation would seem to suggest that the same problem as described above exists here as well for the radial coordinate r . If we substitute the Hamiltonian above into the relation $\langle r \cdot \partial H / \partial r \rangle = k_B T$, we obtain for the average potential energy $\langle m \omega^2 r^2 / 2 \rangle = k_B T / 2$, i.e., only half of the correct average potential energy for this system. The trivial solution, in this case, is that we are mixing different sets of canonical coordinates. The Hamiltonian in Eq. (5) is expressed most straightforwardly in terms of the coordinates $\{x, y, p_x, p_y\}$; if we wish to apply the theorem to the variable $r = \sqrt{x^2 + y^2}$, we must express the Hamiltonian in terms of a consistent set of polar coordinates: $H = H(r, \theta, p_r, p_\theta)$. Let us see how this standard transformation solves this initial puzzle.

A. Polar coordinates in configuration space

The starting point is the usual transformation from rectangular to polar coordinates in configuration space

$$\begin{aligned} r &\equiv \sqrt{x^2 + y^2}, \quad \text{with } r \in [0, \infty), \\ \theta &\equiv \tan^{-1}\left(\frac{y}{x}\right), \quad \text{with } \theta \in [0, 2\pi]. \end{aligned} \quad (6)$$

We now need to determine the corresponding transformation of momentum coordinates (p_x, p_y) , so that the whole transformation is a canonical one (the GET concerns canonical sets of coordinates). The change of variables is most conveniently carried out starting from the Lagrangian, but we will instead use the generating function formalism,¹⁰ in preparation for the analysis of the free particle.

The generating function approach is based on noticing that the relation between the old (q_i, p_i) canonical coordinates (with Hamiltonian $H(q_i, p_i)$) and the new ones (Q_j, P_j) (with “Kamiltonian” $K(Q_j, P_j)$) has the form

$$p_i \dot{q}_i - H = P_j \dot{Q}_j - K + \frac{\partial F}{\partial t}, \quad (7)$$

where F is a “generating” function that depends on a certain subset of both old and new coordinates. (A summation convention over repeated indexes is assumed here and below.)

The present case belongs to the important class of point transformations for which the new coordinates depend only on the old coordinates and time, i.e., $Q_j = f_j(q; t)$ (where q is used as shorthand for $\{q_1, q_2, \dots\}$). As shown below, in this case the generating function that connects the two sets of coordinates is expressed as

$$F = f_j(q; t)P_j - Q_j P_j, \quad (8)$$

where the time dependence has been kept for generality but will be dropped in the following.

Substituting the time derivative of F into Eq. (7), we get

$$p_i \dot{q}_i - H = -K + \frac{\partial f_j(q)}{\partial q_i} \dot{q}_i P_j + f_j(q) \dot{P}_j - Q_j \dot{P}_j, \quad (9)$$

and since the old and new coordinates are separately independent, this relation can hold only if the coefficients of \dot{q}_i and \dot{P}_j vanish,¹⁰ leaving

$$Q_j = f_j(q), \quad (10)$$

$$p_i = \frac{\partial f_j(q)}{\partial q_i} P_j, \quad (11)$$

$$H = K. \quad (12)$$

We therefore recover the general relations between old and new canonical coordinates [Eq. (10)] and, more importantly, we obtain the transformation for the momenta [Eq. (11)]. Finally, Eq. (12) shows that the new Hamiltonian is obtained by simply changing variables in the old one.

Returning to the harmonic oscillator case, by comparing Eq. (10) with Eq. (6), we first identify the set $\{f_j(q)\}$

$$f_r(x, y) = \sqrt{x^2 + y^2}, \quad (13)$$

$$f_\theta(x, y) = \tan^{-1}\left(\frac{y}{x}\right). \quad (14)$$

Armed with these functions, we can then use Eq. (11) to relate the new (p_r, p_θ) to the old (p_x, p_y)

$$p_x = \frac{\partial f_r}{\partial x} p_r + \frac{\partial f_\theta}{\partial x} p_\theta = \cos(\theta) p_r - \frac{\sin(\theta)}{r} p_\theta, \quad (15)$$

$$p_y = \frac{\partial f_r}{\partial y} p_r + \frac{\partial f_\theta}{\partial y} p_\theta = \sin(\theta) p_r + \frac{\cos(\theta)}{r} p_\theta. \quad (16)$$

Substituting these expressions into Eq. (5), and considering the identity (12), we get for the Hamiltonian

$$H = \frac{1}{2m} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{1}{2} m \omega^2 r^2, \quad (17)$$

which is the same expression that one would find using the more familiar Lagrangian technique.

It is the term with an inverse dependence on r^2 that saves the GET. First, we apply the GET to the p_θ coordinate,

$$k_B T = \left\langle p_\theta \cdot \frac{\partial H(p_r, p_\theta, r, \theta)}{\partial p_\theta} \right\rangle = \left\langle \frac{p_\theta^2}{mr^2} \right\rangle. \quad (18)$$

Next we do the same for the r variable,

$$k_B T = \left\langle r \cdot \frac{\partial H(p_r, p_\theta, r, \theta)}{\partial r} \right\rangle = - \left\langle \frac{p_\theta^2}{mr^2} \right\rangle + \langle m \omega^2 r^2 \rangle. \quad (19)$$

Adding these two results and dividing by 2, we obtain

$$\frac{1}{2} \langle m \omega^2 r^2 \rangle = k_B T, \quad (20)$$

as expected (but at variance with the result $k_B T/2$ obtained with a sloppy manipulation). The key was to use a consistent set of coordinates for the Hamiltonian.

B. Polar coordinates in momentum space

We now turn to the kinetic energy part of the harmonic oscillator Hamiltonian, which gave rise to a paradoxical situation in the free particle case (when expressed in terms of the momentum modulus, $H = p^2/2m$). Because we need to work with a canonical set of coordinates that includes p , we define a transformation to polar coordinates in momentum space

$$\begin{aligned} p &\equiv \sqrt{p_x^2 + p_y^2}, \quad \text{with } p \in [0, \infty), \\ \Theta &\equiv \tan^{-1}\left(\frac{p_y}{p_x}\right), \quad \text{with } \Theta \in [0, 2\pi]. \end{aligned} \quad (21)$$

As before, we need to determine the corresponding transformation of the spatial coordinates (x, y) . Following the generating function methodology, we note that taking $F = q_i p_i - g_j(p) Q_j$, we get the relations

$$P_j = g_j(p), \quad (22)$$

$$q_i = \frac{\partial g_j(p)}{\partial p_i} Q_j. \quad (23)$$

From Eq. (21) we identify the functions $g_j(p_i)$ that define the new “momenta” (p, Θ) in terms of the old ones (p_x, p_y)

$$g_p(p_x, p_y) = \sqrt{p_x^2 + p_y^2}, \quad (24)$$

$$g_\Theta(p_x, p_y) = \tan^{-1}\left(\frac{p_y}{p_x}\right). \quad (25)$$

The new (Q_p, Q_Θ) and old (x, y) “position” coordinates are related using Eq. (23)

$$\begin{aligned} x &= \frac{\partial g_j}{\partial p_x} Q_j = \frac{\partial g_p}{\partial p_x} Q_p + \frac{\partial g_\Theta}{\partial p_x} Q_\Theta \\ &= \cos(\Theta) Q_p - \frac{\sin(\Theta)}{p} Q_\Theta, \\ y &= \frac{\partial g_j}{\partial p_y} Q_j = \frac{\partial g_p}{\partial p_y} Q_p + \frac{\partial g_\Theta}{\partial p_y} Q_\Theta \\ &= \sin(\Theta) Q_p + \frac{\cos(\Theta)}{p} Q_\Theta, \end{aligned} \quad (26)$$

with inverse relations

$$\begin{aligned} Q_p &= \cos(\Theta)x + \sin(\Theta)y, \\ Q_\Theta &= -p \sin(\Theta)x + p \cos(\Theta)y. \end{aligned} \quad (27)$$

Substituting Eq. (26) into the harmonic oscillator Hamiltonian, we obtain

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 \left(Q_p^2 + \frac{Q_\Theta^2}{p^2} \right), \quad (28)$$

which in retrospect was to be expected by simple symmetry arguments, when compared with Eq. (17).

It is the term inversely proportional to p^2 that allows the GET to be valid for p in this case. Starting from

$$\left\langle p \cdot \frac{\partial H(p, \Theta, Q_p, Q_\Theta)}{\partial p} \right\rangle = k_B T, \quad (29)$$

and considering the symmetry between Hamiltonians Eqs. (28) and (17), an argument that parallels that of Eqs. (18) and (19) leads to the expected result

$$\left\langle \frac{p^2}{2m} \right\rangle = k_B T, \quad (30)$$

or $k_B T/2$ for each Cartesian component.

To summarize, in the case of the harmonic oscillator the GET is perfectly valid for the modulus of the momentum (p) . However, for our argument it was essential that a (harmonic) confining potential was present in the Hamiltonian.

III. BREAKDOWN FOR A FREE PARTICLE

It is now time to return to the result obtained in the Introduction for a free particle [see Eq. (4)], which stands in strong contrast with Eq. (30). A literal interpretation of the GET cannot possibly be valid for p in the free particle case, even though all the usual requirements are fulfilled.

It should be clear by now that for the free Hamiltonian,

$$H = \frac{p^2}{2m}, \quad (31)$$

no canonical change of coordinates can bring up a term similar to the one with an inverse dependence on p^2 that we just obtained for the harmonic oscillator, so that we might recover Eq. (30).

The origin of the problem lies in the somewhat loose statement of the conditions required for the validity of the GET, specifically with regard to the interaction with the confining walls. Let us review the usual derivation of the GET in the canonical ensemble. We write the integral over all phase space variables as $\int d\omega$, and, as in Eq. (1), denote the variable of interest as x_i . We also define $\omega(i)$ as the set of all phase space variables except x_i . Isolating the x_i integral and then performing an integration by parts (with the change of variables $u \equiv x_i$, $dv \equiv (\partial H / \partial x_i) e^{-\beta H} dx_i$),^{1,3} we obtain

$$\begin{aligned} \left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle &= \frac{1}{Z} \int x_i \frac{\partial H}{\partial x_i} e^{-\beta H} d\omega, \\ &= \frac{1}{Z} \int d\omega(i) \left\{ x_i \frac{\partial H}{\partial x_i} e^{-\beta H} dx_i \right\}, \\ &= \frac{k_B T}{Z} \int d\omega(i) \left\{ [-x_i e^{-\beta H}]_{x_{i1}}^{x_{i2}} + \int e^{-\beta H} dx_i \right\}, \end{aligned} \quad (32)$$

where $\beta = 1/(k_B T)$ and x_{i1} and x_{i2} denote the extreme values of coordinate x_i . For the validity of the theorem, it is necessary that the boundary term $-x_i e^{-\beta H}$ cancels out when evaluated at its two limits (x_{i2} and x_{i1}). From this condition, we easily recover the conditions initially stated regarding the acceptable limiting behavior: x_i becomes either zero or infinity at its two limits, and the energy becomes infinite if x_i does.

What is usually not stated is that, in addition, it is assumed that the limits for the rest of the coordinates are independent of x_i . If such a dependence exists we cannot isolate the integration over the variable x_i as we have done above—before proceeding with the integration over x_i , one must integrate out the variables whose limits depend on it.

Let us now see in detail that this is actually the explanation in the present case, and that when using a set of generalized coordinates for which p is one of the members, we actually obtain the correct answer (in the particular case of a free particle in a two-dimensional box)

$$\left\langle p \frac{\partial H}{\partial p} \right\rangle = 2k_B T, \quad (33)$$

where the factor of 2 stands in strong contrast with the GET.

Incidentally, there is a simple proof of the correctness of this result using the chain rule

$$p \cdot \frac{\partial H}{\partial p} = \sum_i p \frac{\partial H}{\partial p_i} \frac{\partial p_i}{\partial p} = \sum_i p \frac{\partial H}{\partial p_i} \frac{p_i}{p} = \sum_i \frac{p_i^2}{m}, \quad (34)$$

so that

$$\left\langle p \frac{\partial H}{\partial p} \right\rangle = \left\langle \sum_i \frac{p_i^2}{m} \right\rangle = 2k_B T, \quad (35)$$

since we know the Cartesian momenta (p_i) satisfy equipartition. This procedure, though, might seem to suggest that we

need to go through more “legitimate” canonical coordinates (Cartesian momenta in this case). One would like to show that such a roundabout approach is not required, and that one can stick to the $\{Q_p, Q_\Theta, p, \Theta\}$ coordinates.

As a preamble, let us calculate the partition function of a free particle in a two-dimensional square box of width L , as shown in Fig. 1(a). Using Cartesian coordinates, we have

$$Z = \frac{1}{h^2} \int_0^L dx \int_0^L dy \int_{-\infty}^{\infty} dp_x e^{-\beta p_x^2/2m} \int_{-\infty}^{\infty} dp_y e^{-\beta p_y^2/2m} = \frac{L^2}{\lambda^2}, \quad (36)$$

where $\lambda = h/\sqrt{2\pi m k_B T}$ denotes the thermal wavelength. As stated in the introduction, the GTE is perfectly valid for the Cartesian components of the momentum in the free case; for instance,

$$\left\langle p_x \frac{\partial H}{\partial p_x} \right\rangle = \frac{1}{Z} \frac{1}{h^2} \int_0^L dx \int_0^L dy \int_{-\infty}^{\infty} dp_x \frac{p_x^2}{m} e^{-\beta p_x^2/2m} \times \int_{-\infty}^{\infty} dp_y e^{-\beta p_y^2/2m} = k_B T. \quad (37)$$

Let us now see what is obtained with the set of generalized coordinates $\{Q_p, Q_\Theta, p, \Theta\}$, defined in Sec. II. Again, we

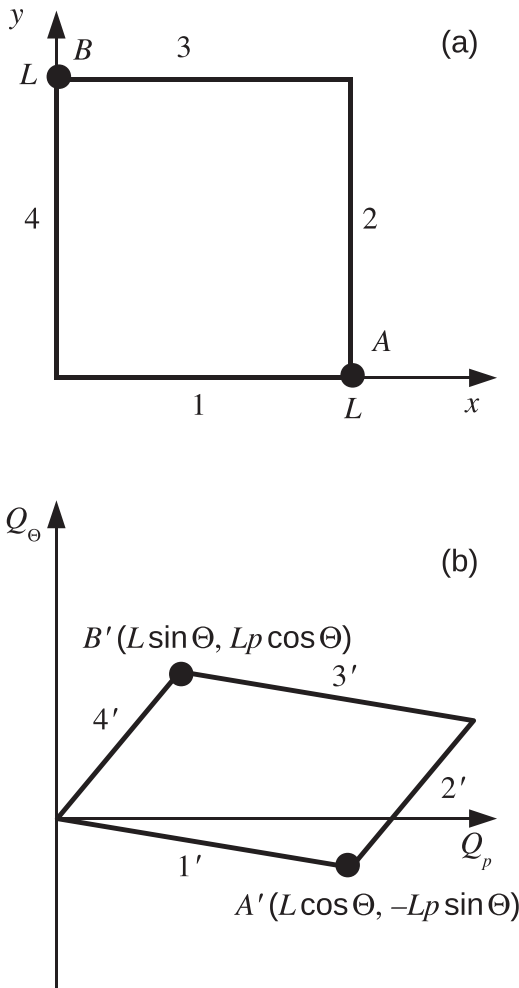


Fig. 1. (a) Domain in real space (x, y) , for calculating the partition function of a free particle confined to a square box; (b) The corresponding domain in (Q_p, Q_Θ) space, where A' and B' denote the two vectors used to compute the area of the parallelogram.

start from the computation of the partition function. We already know the limits of integration for (p, Θ) [see Eq. (21)], so our only remaining task is to determine the domain of integration for the variables (Q_p, Q_Θ) . A sketch is displayed in Fig. 1(b).

We will illustrate the procedure for the transformation of the boundary that in xy -space is defined by the lowest horizontal line (i.e., $y=0, x \in [0, L]$), and leave the rest of the calculation for the Appendix. Using Eq. (27), we have $Q_p = x \cos(\Theta)$ and $Q_\Theta = -xp \sin(\Theta)$, from which we see that the new boundary is also described by a straight line: $Q_\Theta = -p \tan(\Theta) Q_p$. In this way, the original square is distorted, as shown in Fig. 1(b). The new shape is a parallelogram, whose total area is (see the Appendix)

$$\int dQ_p \int dQ_\Theta = L^2 p. \quad (38)$$

We now see how the dependence on p of the boundary conditions for (Q_p, Q_Θ) forbids any direct integration by parts of this variable, prior to the integration in the (Q_p, Q_Θ) domain. No such issue arose with the Cartesian components.

Using Eq. (38), we can now evaluate the partition function in our polar coordinate system

$$Z = \frac{1}{h^2} \int_0^\infty dp \int_0^{2\pi} d\Theta \int dQ_p \int dQ_\Theta e^{-\beta p^2/2m} = \frac{2\pi L^2}{h^2} \int_0^\infty dp p e^{-\beta p^2/2m} = \frac{L^2}{\lambda^2}, \quad (39)$$

in agreement with Eq. (36). (This procedure surely qualifies as one of the most convoluted possible derivations of the simplest multidimensional partition function!)

It is now straightforward to compute $\langle p \partial H / \partial p \rangle$ in $\{Q_p, Q_\Theta, p, \Theta\}$ space

$$\left\langle p \frac{\partial H}{\partial p} \right\rangle = \left\langle \frac{p^2}{m} \right\rangle = \frac{\int_0^\infty dp p (p^2/m) e^{-\beta p^2/2m}}{\int_0^\infty dp p e^{-\beta p^2/2m}} = 2k_B T, \quad (40)$$

where the integrals over Q_p, Q_Θ , and Θ are not shown because they cancel between the numerator and denominator. This is the result we wanted to prove. In short, although the conditions usually assumed for the canonical coordinate are met, the GET does not hold due to the dependence of the integration limits of other coordinates on the coordinate of interest (p).

IV. BOUNDARY CONDITIONS VERSUS CONFINING POTENTIALS

From a physical standpoint, the origin of the problem has to do with the nature of the confining walls. The two simple examples we have been working with (harmonic oscillator and free particle) illustrate this. On one hand, the isotropic harmonic potential is an example of a soft confining potential, and we have seen that it poses no problem for the GET. On the other hand, a free particle with walls defined by boundary conditions corresponds to an idealized hard

confining potential, and here is where we have found that the GET fails (although it does not for the Cartesian components).

It turns out that, in this particular instance, the result for hard walls is different from what we would find by taking the limit of increasingly hard smooth confining potentials. To illustrate this point, let us consider the sequence of (isotropic) potentials

$$H = \frac{1}{2m} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{1}{2} k_n r^n, \quad (41)$$

parametrized by the exponent n , which we take to be a positive even integer. As $n \rightarrow \infty$ the confining potential tends to be steeper at large r and flatter at points closer to the origin. In this way, we are mimicking a round container with the interactions progressively confined at the boundary and, concomitantly, a larger area that is almost interaction free. The goal is to see that as $n \rightarrow \infty$ the GET is valid for the p coordinate at all times, while at the same time the average potential energy associated to the interaction with the walls tends to zero, as one expects from increasingly hard walls.

For p_θ nothing has changed from the isotropic harmonic oscillator, so Eq. (18) continues to be valid. But in the radial coordinate, a factor of n appears⁴

$$k_B T = \left\langle r \cdot \frac{\partial H}{\partial r} \right\rangle = - \left\langle \frac{p_\theta^2}{mr^2} \right\rangle + \left\langle \frac{n}{2} k_n r^n \right\rangle, \quad (42)$$

from which we get

$$\left\langle \frac{1}{2} k_n r^n \right\rangle = \frac{2}{n} k_B T, \quad (43)$$

which tends to zero for $n \rightarrow \infty$ as expected.

As for the momentum modulus, the Hamiltonian is now

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 \left(Q_p^2 + \frac{Q_\Theta^2}{p^2} \right)^n, \quad (44)$$

and it is straightforward to check that applying the GET,

$$\left\langle p \cdot \frac{\partial H}{\partial p} \right\rangle = k_B T, \quad (45)$$

we obtain

$$\left\langle \frac{p^2}{2m} \right\rangle = k_B T, \quad (46)$$

independent of the value of n . Therefore, in the presence of a smooth confining potential the GET is restored for the p coordinate, although this potential can be made arbitrarily hard.

This result does not depend on the use of a particular sequence of potentials. It can be obtained generally with the help of the canonical transformations that have served us so well. Let us consider a generic position-dependent confining potential $U(x, y)$, so that the Hamiltonian is

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + U(x, y). \quad (47)$$

We now follow the same route as in Eq. (34), with the difference that we also need to consider the potential energy derivatives with respect to p , for which we need to recall relations (26)

$$\begin{aligned} p \frac{\partial H}{\partial p} &= p \left\{ \frac{\partial H}{\partial p_x} \frac{\partial p_x}{\partial p} + \frac{\partial H}{\partial p_y} \frac{\partial p_y}{\partial p} + \frac{\partial H}{\partial x} \frac{\partial x}{\partial p} + \frac{\partial H}{\partial y} \frac{\partial y}{\partial p} \right\}, \\ &= \frac{p_x^2}{m} + \frac{p_y^2}{m} + p \frac{\partial U}{\partial x} \frac{\partial x}{\partial p} + p \frac{\partial U}{\partial y} \frac{\partial y}{\partial p}, \\ &= \frac{p_x^2}{m} + \frac{p_y^2}{m} + \frac{\partial U}{\partial x} [-\sin(\Theta)x + \cos(\Theta)y] \sin(\Theta) \\ &\quad + \frac{\partial U}{\partial y} [\sin(\Theta)x - \cos(\Theta)y] \cos(\Theta). \end{aligned} \quad (48)$$

If we now average this formula (considering that averages over positions x, y and momenta Θ are independent), we obtain the desired validity of the GET for the momentum modulus

$$\begin{aligned} \left\langle p \cdot \frac{\partial H}{\partial p} \right\rangle &= \left\langle \frac{p_x^2}{m} \right\rangle + \left\langle \frac{p_y^2}{m} \right\rangle \\ &\quad - \left\langle x \frac{\partial U}{\partial x} + y \frac{\partial U}{\partial y} \right\rangle \langle \sin^2(\Theta) \rangle \\ &= 2k_B T - (2k_B T) \cdot \frac{1}{2} = k_B T, \end{aligned} \quad (49)$$

where we have assumed only that $U(x, y)$ is sufficiently well behaved^{3,7} so that we can apply the GET to positional coordinates

$$\left\langle x \frac{\partial U}{\partial x} \right\rangle = \left\langle y \frac{\partial U}{\partial y} \right\rangle = k_B T. \quad (50)$$

V. CONCLUDING REMARKS

It has been well-known, since its initial formulation,⁹ that the inclusion of the interaction with confining walls guarantees that the GET is satisfied for *spatial* coordinates. This was made more explicit in subsequent textbook expositions,³ and discussed in detail in Ref. 7. What it is shown here is that for the theorem to be valid for the *momentum* modulus, and in contrast with what one might expect, special care must be taken as well with the handling of confining walls. Basically, the GET in its usual formulation fails for ideal hard confining walls (defined as those represented by boundary conditions). The theorem recovers its validity, though, if the confining walls are described instead by a smooth potential. A similar statement could be made for the more specific theorem of equipartition (TE) for quadratic contributions to the Hamiltonian.

From a more practical point of view, one should be cautious with the use of a Hamiltonian that does not include an explicit interaction with walls (in addition to any inter-particle interactions). While some quantities, such as momentum Cartesian components, pose no problems (and these are the ones usually manipulated in textbooks), others require the consideration of more physically reasonable walls (or a different form of the GTE, like Eq. (35), which does not seem advisable). Finally, although we have focused

on free particles, similar considerations would be applicable to the center-of-mass momentum modulus for a system of interacting particles.

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APPENDIX: INTEGRATION OF CONJUGATE COORDINATES

Here, it is shown how the square displayed in Fig. 1(a) is transformed into the parallelogram in Fig. 1(b), under the effect of the canonical transformation to polar coordinates in momentum space, Eqs. (21) and (27). The set of segments (1, 2, 3, 4) is transformed into (1', 2', 3', 4'), which will be addressed in turn.

- Segment 1: Somewhat expanding on the succinct explanation given in Sec. III, in this case we have $y=0$, which if substituted into Eq. (27), results in the relations $Q_p = x \cos(\Theta)$ and $Q_\Theta = -xp \sin(\Theta)$. Taken together, the boundary (1') in (Q_p, Q_Θ) space is now defined by the linear relation $Q_\Theta = -p \tan(\Theta) Q_p$. The initial and final points in (x, y) space, namely, (0,0) and (L,0) [point A in Fig. 1(a)], are now, respectively, transformed into (0, 0) and $(L \cos(\Theta), -Lp \sin(\Theta))$ (point A' in Fig. 1(b)).
- Segment 2: Now we have $x=L$, which results in the relations $Q_p = L \cos(\Theta) + y \sin(\Theta)$, $Q_\Theta = yp \cos(\Theta) - Lp \sin(\Theta)$. When these are combined, we have again a linear relation: $Q_\Theta = pQ_p / \tan(\Theta) - pL / \sin(\Theta)$. This straight line (2') has end points at $(L \cos(\Theta), -Lp \sin(\Theta))$ and $(L \cos(\Theta) + L \sin(\Theta), Lp \cos(\Theta) - Lp \sin(\Theta))$.
- Segment 3: The constraint $y=L$ now results in $Q_p = x \cos(\Theta) + L \sin(\Theta)$ and $Q_\Theta = Lp \cos(\Theta) - xp \sin(\Theta)$.

The linear relation is now $Q_\Theta = -p \tan(\Theta) Q_p + Lp / \cos(\Theta)$, so that segment 3' has the same slope as segment 1'. The end points are $(L \cos(\Theta) + L \sin(\Theta), Lp \cos(\Theta) - Lp \sin(\Theta))$ and $(L \sin(\Theta), Lp \cos(\Theta))$ (B' in Fig. 1(b)).

- Segment 4: Now $x=0$ results in $Q_p = y \sin(\Theta)$ and $Q_\Theta = yp \sin(\Theta)$, so we get $Q_\Theta = pQ_p / \tan(\Theta)$. Segment 4' has the same slope as segment 2', with end points $(L \sin(\Theta), Lp \cos(\Theta))$ and (0, 0), and therefore the resulting figure is a parallelogram.

The surface area of the parallelogram can be computed as the modulus of the determinant constructed from the vectors that are directed from the origin to points A' and B', respectively,

$$\int dQ_p \int dQ_\Theta = \begin{vmatrix} L \cos(\Theta) & L \sin(\Theta) \\ -Lp \sin(\Theta) & Lp \cos(\Theta) \end{vmatrix} = L^2 p. \quad (\text{A1})$$

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